REMOVAL OF ISOPROTURON FROM AQUEOUS SOLUTION BY ZSM-5 ZEOLITE

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Abstract

ZSM-5 zeolite was used to remove isoproturon pesticide from aqueous solutions. The main parameters of adsorption process such as dosages of adsorbent, contact time and initial concentration of isoproturon were investigated. Adsorption equilibrium studies were carried out in batch systems. Results were modeled by adsorption isotherms: Langmuir, Freundlich and Temkin isotherms. The best correlation was achieved with Temkin adsorption isotherm. The maximum adsorption capacity of isoproturon calculated from the Langmuir isotherm was 4,12 mg g^{-1} at room temperature. Adsorption kinetics of isoproturon has been studied by commonly used kinetic models, i.e., the pseudo-first-order model, the pseudo-second-order model and the intraparticle diffusion model. The kinetic modeling studies showed that kinetics of isoproturon on Zeolite ZSM-5 followed the model of pseudo - second order. This study proved that ZSM-5 zeolite could be used for the removal of isoproturon from aqueous media.

Introduction

Pesticides and herbicides, intentionally released into the environment, are ubiquitous in aquatic systems; they are often detected at low levels and commonly occur in the form of complex mixtures [1-2]. Leaching of chemical fertilizers and pesticides, applied to agricultural and forest land, is one of the main reasons for organic pollution in several water streams. Pesticides and herbicides are harmful to life because of their toxicity, carcinogenicity and mutagenicity [3].

Isoproturon, which belongs to phenylurea herbicides, is slowly degraded in water and quite persistent [4]. Although, there are so far no reported incidences of human poisoning, based on effects seen in animals, acute exposure to isoproturon would be expected to cause mild skin irritation and headaches, drowsiness, and lack of coordination. Thus, the efforts of many researchers have been focused on developing new and efficient remediation treatments to clean this phenylurea herbicide from the environment [4].

It has been proven that the adsorption is considered as an attractive method for the removal of different organic pollutants from environmental matrices due to its simplicity and ease of operation over other physical, biological and chemical technologies like precipitation followed by coagulation [5], membrane filtration [6-7] and photochemical degradation [8]. Natural adsorbents such as charcoal, clay minerals or zeolites are, in many instances relatively cheap, abundant in supply and have significant potential for modification of their adsorption capabilities.

The main propose of this study is to investigate the influence of factors such as contact time, mass of adsorbent ZSM-5 and initial concentration of selected pesticide isoproturon on the removal of isoproturon from aquatic media.

Material and methods

All chemicals used were of analytical grade. Stock standard solution of isoproturon (200 ppm) has been prepared by dissolving 5 mg of analytical standard in 25 mL of methanol. The stock solution was then appropriately diluted to get the test solutions.

All glassware were cleaned, then rinsed with deionised water and dried at 60 °C in a temperature controlled oven. Measurements were conducted at the room temperature (25 ± 2 °C). Zeolite ZSM-5 (manufacturer Acros Organics, Geel, Belgium) was used as adsorbent. Zeolite ZSM-5 has a very high temperature and acid stability (>1000 °C and down to pH=3, respectively). It is synthesized at high temperatures and pressures in an autoclave coated with Teflon and is characterized by low water solubility. Zeolite ZSM-5 is a type of a "high-silica"-Zeolite, which is responsible for most of its special properties. Total surface area (BET) of ZSM-5 is 390 m^2g^{-1}.

The experiments were carried out by varying concentrations of initial isoproturon solution, contact time and amount of adsorbent. Adsorption measurements were determined by batch experiments of known amount of the sample with 50 mL of aqueous isoproturon solutions in a series of 150 mL glass flasks. The mixtures were shaken at a constant temperature on orbital shaker at 140 rpm at room temperature for a given time. The suspensions were filtered and the filtrates were analyzed using HPLC-DAD (1260, Agilent Infinity). Separation was performed with a reversed phase column Eclipse XDB-C18 (3 x 150 mm, particle size 3.5µm). The operating conditions were: the flow of 0.8 $mLmin^{-1}$, the temperature of the column was 25 C° and injection volume of 10 µL. The isocratic separation with the ratio of mobile phases of 50:50 (water and acetonitrile) was used. The maximum wavelength of 255 nm was used for determination of isoproturon concentration. Retention time of isoproturon was 5 min.

Adsorbed amount, qe (mg g^{-1}), was calculated via the equation:

$$qe = \frac{(C_{\circ} - C_f\ )}{m} * V \qquad (1)$$

where q_e is the adsorption capacity (mg g^{-1}), C_0 and C_f are the initial and final isoproturon concentrations, respectively (expressed in mg L^{-1}), V is the solution volume (mL) and m is the adsorbent dosage (g).

The adsorption isotherms of isoproturon on zeolite were studied at room temperature, three widely used models: Langmuir, Freundlich and Temkin were applied for the fitting of the experimental data. The kinetic of the adsorption data was analyzed using three different kinetic models: the pseudo-first order, pseudo-second-order and intraparticle diffusion models.

The pseudo-first-order kinetic has been widely used to predict sorption kinetics, expressed by the following equation:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2{,}303}\right)\mathrm{t} \qquad (2)$$

where k_1 (1 min^{-1}) is the equilibrium rate constant of the pseudo-first order adsorption and it is determined from the plot of log $(q_e - q_t)$ as a function of *t*.

The pseudo-second-order model can be represented in the following form:

$$\frac{t}{q_t} = \frac{1}{k_2 . q_e^2} + \frac{1}{q_e} t \qquad (3)$$

By plotting t/qt versus t, qe and k_2 can be determined from slope and intercept, where k_2 (g mg $^{-1}$ min^{-1}) is the pseudo-second order rate constant.
The rate parameter of intraparticle diffusion can be defined as:

$$q_t = k_{id} \cdot t^{1/2} + C \qquad (4)$$

where q_t is the amount of pesticide adsorbed at time t, C the intercept and k_{id} (mg g^{-1} min $^{-1/2}$) is the intraparticle diffusion rate constant.

Results and discussion

Influence of mass of ZSM-5 was studied with isoproturon concentration of 5 mgL^{-1} and contact time of 60 min. Different masses of zeolite were tested: 150, 200, 250, 300 and 350 mg. Results indicated the removal range from 90,6 to 92,7 %. There was no significant difference in removal efficiency and ZSM-5 mass of 150 mg was used for further analyses.
The adsorption kinetics of isoproturon was evaluated for the initial concentration of 5 mgL^{-1} and ZSM-5 mass of 150 mg. The mixing procedure was carried out with fixed speed (140 rpm) for the periods of 5, 10, 20, 30, 60 and 90 minutes. Removal efficiency ranged from 71.7 % to 91,2 % and increased with increasing of contact time till 60 min, then reached equilibrium. Three kinetic models were tested: pseudo first-order model, pseudo second-order model and intraparticle diffusion model (Table 1).

Table 1. Kinetic parameters for the adsorption of isoproturon onto ZSM-5

Pseudo-first order	q_e (mg g^{-1}) k_1 (min^{-1}) r	0.71 0.06 0.98
Pseudo-second order	q_e (mg g^{-1}) k_2 (g mg^{-1}.min^{-1}) r	2.34 0.18 0.99
Intraparticle diffusion	k_{id} (mg g^{-1} min$^{-1/2}$) C (mg g-1) r	0.13 1.60 0.92

From the obtained results, it could be concluded that adsorption kinetics of isoproturon on zeolite ZSM-5 could be explained by the pseudo second-order kinetic model.
Influence of initial pesticide concentration on removal of isoproturon from aqueous media was tested with concentrations of 2, 4, 5, 6, 8 and 10 mgL^{-1}, for 150 mg of zeolite and contact time of 60 min. The adsorption process was modeled by Freundlich, Langmuir and Temkin isotherms. Based on the obtained correlation coefficients, the fit of isoproturon adsorption on ZSM-5 is better with Temkin model than with Langmuir and Freundlich model. Figure 1. presents Temkin adsorption isotherm of isoproturn removal on zeolite. According to the Langmuir's model, adsorption capacity for isoproturon on ZSM-5, amounted to 4,12 mg g^{-1}.

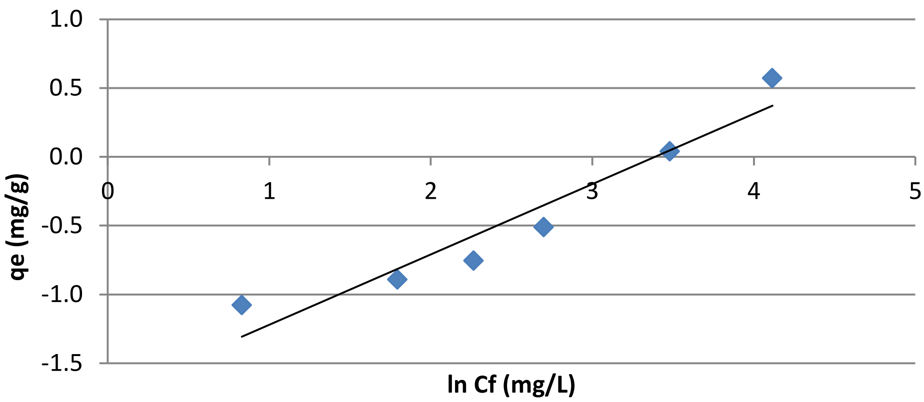

Figure 1. Temkin adsorption isotherm of isoproturon removal on ZSM-5

Conclusion

The ability of zeolite ZSM-5 to remove isoproturon from aqueous solution was investigated. In order to optimize removal process, some of main conditions were taken into account such as: initial concentration of isoproturon, contact time and mass of adsorbent ZSM-5. Those parameters were modeled by Langmuir, Freundlich and Temkin isotherms. The equilibrium studies proved that Temkin isotherm model best describes the adsorption of isoproturon on zeolite. The kinetic modeling studies showed that kinetics of isoproturon on zeolite ZSM-5 followed the model of pseudo - second order. This model includes the assumption that the binding of the particles to the adsorbent surface occurs by establishing specific chemical bonds. From the results of the present work, it can be said that ZSM5 showed quite good capabilities in removing isoproturon pesticide from water.

Acknowledgements

Authors would like to thank Ministry of Education, Science and Technological Development of the Republic of Serbia for financial support (Project No. III46009). Ali Mohammed Hgeig would like to thank the Ministry of Higher Education in Libya for his PhD grant supporting this research.

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